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CORROSION OF ALUMINIDES BY MOLTEN NITRATE SALT*

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Abstract

The corrosion of titanium-, iron-, and nickel-based aluminides by a highly aggressive, oxidizing $NaNO_3$(-KNO_3)-Na_2O_2 has been studied at 650°C. It was shown that weight changes could be used to effectively evaluate corrosion behavior in the subject nitrate salt environments provided these data were combined with salt analyses and microstructural examinations. The studies indicated that the corrosion of relatively resistant aluminides by these nitrate salts proceeded by oxidation and a slow release from an aluminum-rich product layer into the salt at rates lower than that associated with many other types of metallic materials. The overall corrosion process and resulting rate depended on the particular aluminide being exposed. In order to minimize corrosion of nickel or iron aluminides, it was necessary to have aluminum concentrations in excess of 30 at. %. However, even at a concentration of 50 at. % Al, the corrosion resistance of TiAl was inferior to that of Ni_3Al and Fe_3Al. At higher aluminum concentrations, iron, nickel, and iron-nickel aluminides exhibited quite similar weight changes, indicative of the principal role of aluminum in controlling the corrosion process in $NaNO_3$(-KNO_3)-Na_2O_2 salts.

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Introduction

Molten nitrate salts are used as heat transfer fluids for chemical reactions (1), heat treatment baths (1), and coolant and thermal energy storage materials for solar power towers (2). In addition, the chemical properties of nitrate salt can be exploited to produce high purity oxygen and nitrogen gases at a substantial energy savings compared to cryogenic production of oxygen (3). Because of these types of applications and the general scientific interest in these melts, a number of electrochemical and corrosion investigations have been conducted with molten sodium and sodium-potassium nitrate salts (see, for example, refs. 4-18).

The most extensive recent effort in studying corrosion by molten nitrate salts was that of Bradshaw et al. (4-8), who examined stainless steels and alloy 800 in thermal convection loops as well as a variety of materials exposed to static salt. These studies showed that, in general, corrosion resistance was acceptable below 600°C, but above this temperature, significant oxidation and depletion of chromium (due to the high solubility of the chromate ion in the salt) occurred. Whereas the overall corrosion rate was parabolic up to 600°C, nonprotective corrosion behavior (linear kinetics) was evident above 615°C. Results from a related but less detailed study of stainless steels and alloy 800 in thermal convection loops (9) agreed with the findings of Bradshaw et al. At temperatures between 250 and 500°C, iron (10-12), mild steel (13,14), and pure nickel (15) showed passivation characteristics in molten sodium-potassium nitrate salt in association with the formation of oxides consistent with thermodynamic considerations (10-12,16).

The highly oxidizing nature of the nitrate salt at temperatures in excess of about 600°C prompted examination of materials that tend to form stable, protective oxide scales in other environments. Alumina is one such scale and, therefore, selected types of aluminides were exposed to certain nitrate salts under conditions in which steels and other nickel-, cobalt-, and refractory metal-based alloys were severely corroded (18). This paper presents results and analyses from such experiments.

Experimental Procedures

Specimens of selected alumnides were exposed to nitrate salts in alumina crucibles while the melts were continuously sparged with dry air using alumina gas bubbler tubes. Both the crucibles and tubes were replaced after each melt cycle. The specimen was held by a wire (usually 0.5-mm-diam zirconium) and was fully immersed in the salt. Above the salt/gas interface, the other end of the wire was attached to a 6.4-mm-diam nickel rod, which was supported by the compression of an O-ring in one of the end flange fittings. Details of the experimental equipment and procedures are given elsewhere (18). While the gravimetric approach used in this corrosion investigation can be fraught with interpretive difficulties (see Discussion), several studies (17,18) have shown that, with appropriate care, these types of experiments yield adequate figures of merit for judging the relative corrosion resistance of materials exposed to the highly aggressive oxidizing salt environments characteristic of the present work.

Two different nitrate salt base compositions were used in the present study. Salt composition 1A consisted of 49 mol % $NaNO_3$ (44.7% by weight) and 51 mol % KNO_3 (55.3%). Additions of 1 mol % Na_2O_2 (0.85%) were made to obtain the composition 1B. Salt 2A was 100% $NaNO_3$; 0.4 mol % Na_2O_2 (0.4%) was added to 2A to yield 2B. All of the salt components were reagent grade. To facilitate additions to the molten salt during operation, Na_2O_2 was measured into individual containers in an inert atmosphere (to reduce moisture absorption). Single portions were then added to the melt through the crucible vent. The salt in an individual crucible was kept molten between specimen immersions and was replaced with a new charge only after a number of specimens had been exposed.

Table I lists the compositions of the aluminides used for the present study. The aluminide specimens, most of which were iron-based, were taken from sheet material usually worked from small arc-melted heats. Several bulk alumina specimens of high theoretical density were also exposed to the salt. To prepare the specimens, material was sheared or cut as close to the nominal dimensions, 5.1 x 2.5 x 19 mm, as possible. Selected aluminide specimens were lightly etched to remove surface films and then annealed at 850°C in air for 1 h. Final preparation involved surface cleaning using compatible solvents. All dimensional measurements were made with a dial caliper and all weights were measured with an electronic balance to the nearest 0.1 mg.

Table I Compositions of Aluminides Exposed to Molten Nitrate Salt in the Present Study

Material	Composition (at. %)		
	Base	Al	Other
TiAl	50	50	
Ni_3Al	74	25.3	0.5Hf-0.24B
NiAl	50	50	
Fe-26Al	73.5	26	$0.5TiB_2$
Fe-28Al	72	28	
Fe-30Al	70	30	
Fe-35Al	64.5	35	$0.5TiB_2$
Fe-36Al	64.8	35.8	
Fe-40Al	59.8	40	0.2NbC

Upon removal from the salt, specimens were visually inspected and any unusual observations were noted. After cooling in air, the specimens were rinsed in hot water, the wire was removed, and the specimen was again rinsed. After air drying, the specimen weights and dimensions were recorded. The corroded surfaces and polished cross sections of selected specimens were analyzed by optical and scanning electron microscopy and energy dispersive X-ray analysis (EDX). A few corroded and rinsed surfaces were examined by X-ray diffraction. Salt extracted from crucible melts was analyzed for selected elements by atomic absorption spectroscopy.

Results

Weight Changes

As shown in Figure 1, TiAl was considerably more reactive with these nitrate salts than any of the iron or nickel aluminides. This observation is even more significant in view of the general trend that weight losses for the nickel and iron aluminides decreased as the aluminum content of the alloys increased toward 50 at. % (Figure 1). In order to examine the effect of aluminum concentration on corrosion in greater detail, experiments were conducted with a series of Fe-Al binary alloys (with only very small, if any, concentrations of minor alloying elements) ranging from 26 to 40 at. % Al. It was found that the average weight loss of iron aluminide exposed to $NaNO_3$-KNO_3-Na_2O_2 (Salt 1B) at 650°C decreased with increasing aluminum concentration up to 30 at. % Al, but there was no substantial improvement in corrosion resistance above this concentration. These data are shown in Figure 2, which also includes the nickel aluminide data from Figure 1 for comparison. A similar trend with aluminum concentration was observed for the iron aluminides exposed in the $NaNO_3$-Na_2O_2 (Salt 2B) environment.

The influence of salt composition on the corrosion of iron and nickel aluminides was quite pronounced. The presence of Na_2O_2 in the salt increased the short-term corrosiveness of the nitrate mixture. Figure 3 shows this effect for 24-h weight changes of iron aluminides. However, as shown in Figure 4, the peroxide effect was relatively short-lived. No further increase in weight loss after 24 h was noted for Fe-35Al specimens exposed to $(Na,K)NO_3$ that initially contained 1% Na_2O_2, but high weight losses were measured when the Na_2O_2 concentration was refreshed every 24 h during the course of 72-h specimen exposures [Figure 4(a)]. Figure 4(b) shows a similar, but less dramatic, difference when the same experiments were performed for Ni-50Al. The weight losses were also a function of the amount of sodium nitrate. As shown in Figure 3, pure $NaNO_3$ (Salt 2) was more corrosive than $(Na,K)NO_3$ (Salt 1).

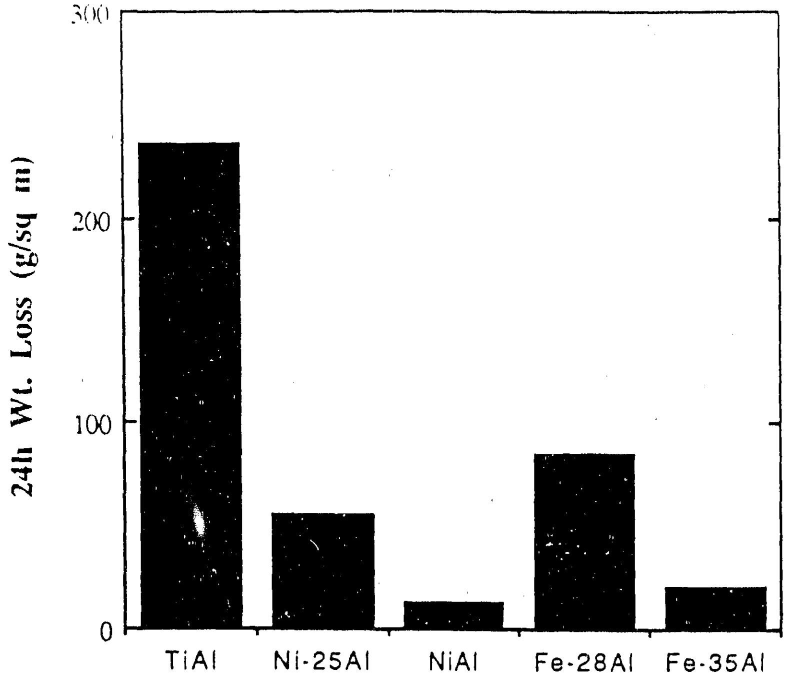

Figure 1 - Average Weight Change in 24 h for Exposure to Salt 1B at 650°C.

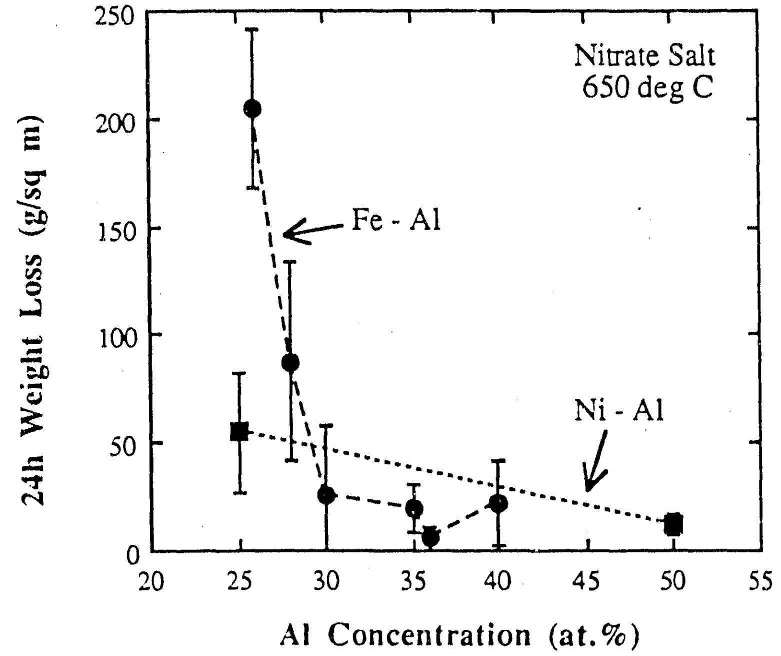

Figure 2 - Average 24-h Weight Changes versus Aluminum Concentration for Exposures in Salt 1B.

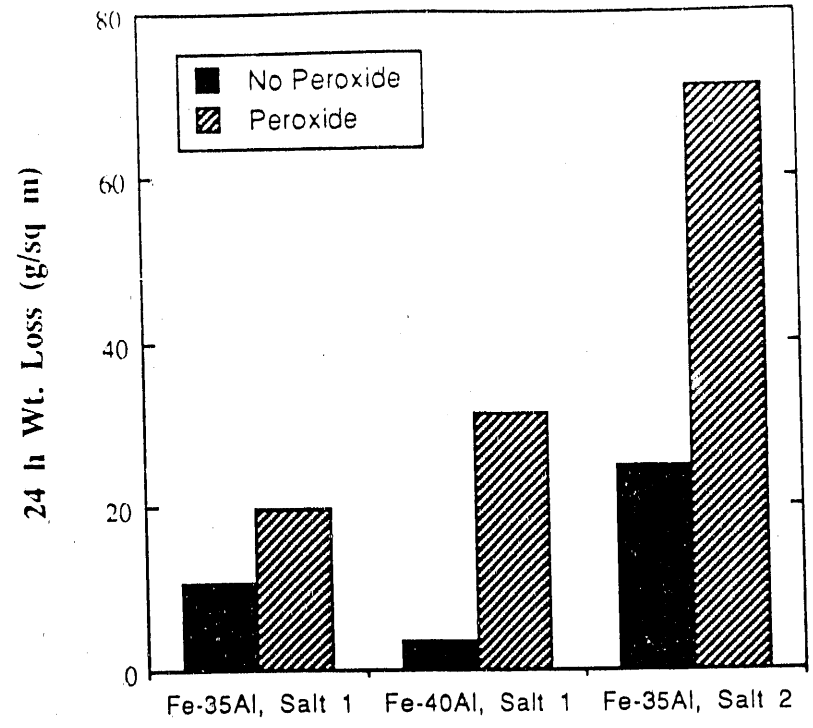

Figure 3 - Average Weight Change for Iron Aluminides Exposed to $NaNO_3$-KNO_3 (Salt 1B) or $NaNO_3$ (Salt 2B) at 650°C for ~24 h (Al concentrations in at. %).

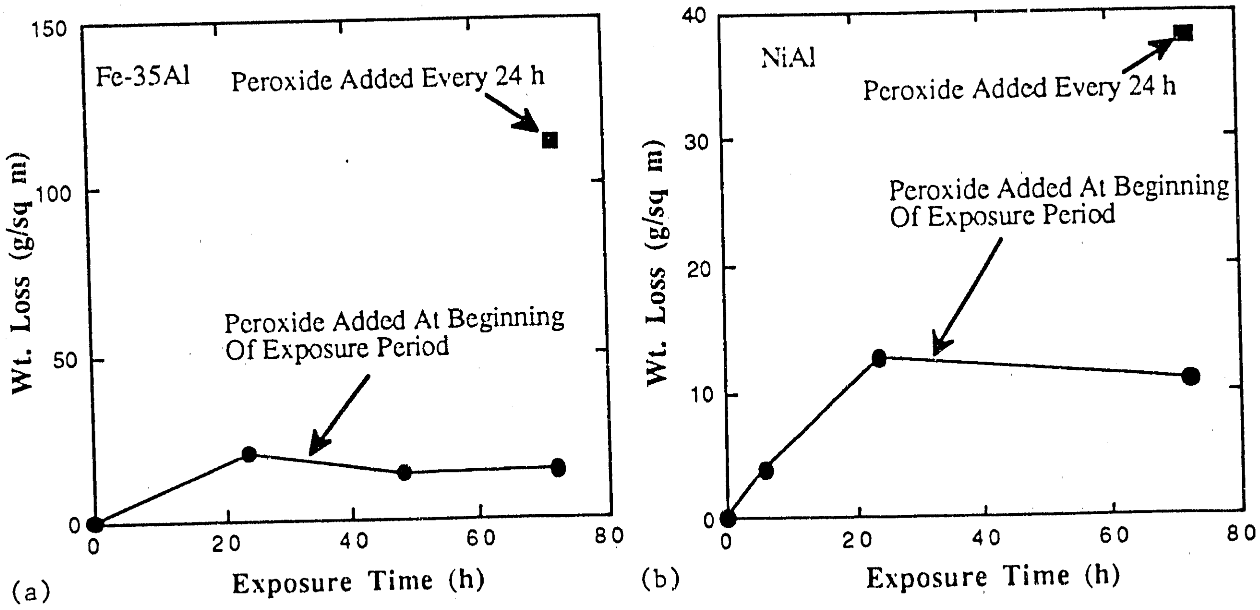

Figure 4 - Weight Loss versus Exposure Time for $NaNO_3$(-KNO_3)-Na_2O_2) at 650°C. (a) Fe-35 at. % Al. (b) NiAl.

As shown in Figure 4, the weight loss kinetics for the iron aluminides correlate with the amount and frequency of Na_2O_2 added during the duration of the exposure. In different experiments, where the same specimen was cleaned and re-exposed to $NaNO_3$-0.4% Na_2O_2 several times, a somewhat similar behavior was observed: the rate of weight loss changed only slightly upon reintroduction of a specimen into the salt if no additional peroxide additions were made, but significantly increased when Na_2O_2 was added. When 0.4% Na_2O_2 was added at the beginning of each incremental exposure period, approximately linear weight loss kinetics and an increasing rate with temperature were observed.

A few specimens of high density, pure bulk alumina were exposed to molten nitrate salt. The measured weight changes, shown in Table II (which also contains data for Fe-35Al and NiAl for comparison), indicated fairly good resistance to corrosion by the salts. The mechanical integrity and low porosity of these alumina specimens were important in determining their corrosion behavior. High weight losses were observed for several other types of bulk ceramics due to uptake of salt into matrix porosity and subsequent crumbling of the surface region.

Table II Comparison of Weight Losses of Alumina and Iron and Nickel Aluminides Exposed to Molten Nitrate Salt for Approximately 24 h

Material	Weight Change (g/m^2)	
	Salt 1B	Salt 2B
Al_2O_3	-2.0[a]	-8.2 ± 2.7[b]
Al_2O_3[c]		-11.0
Fe-35Al	-19.6 ± 10.8	-70.9 ± 28.3
NiAl	-12.6 ± 5.1	

[a] Single crystal.

[b] Includes data for gel-cast alumina with 0 and 0.05 wt % MgO.

[c] Fine grain (2 μm) alumina with 0.1 wt % MgO.

Microstructural Analysis

SEM micrographs of specially (dry) polished cross sections of both as-wrought and preoxidized Ni_3Al exposed to Salt 1 at 650°C for about 48 h are shown in Figure 5. [The specimens shown in this figure were exposed elsewhere (17), but under similar conditions to those described above.] Associated EDX showed that a thin surface layer on both specimens was enriched in aluminum relative to the unaffected underlying matrix and also contained some sodium. The intergranular oxidation seen in Figure 5(b) was not due to the salt exposure, but rather to the high temperature preoxidation treatment (1050°C in air, 24 h), as described by others (19,20).

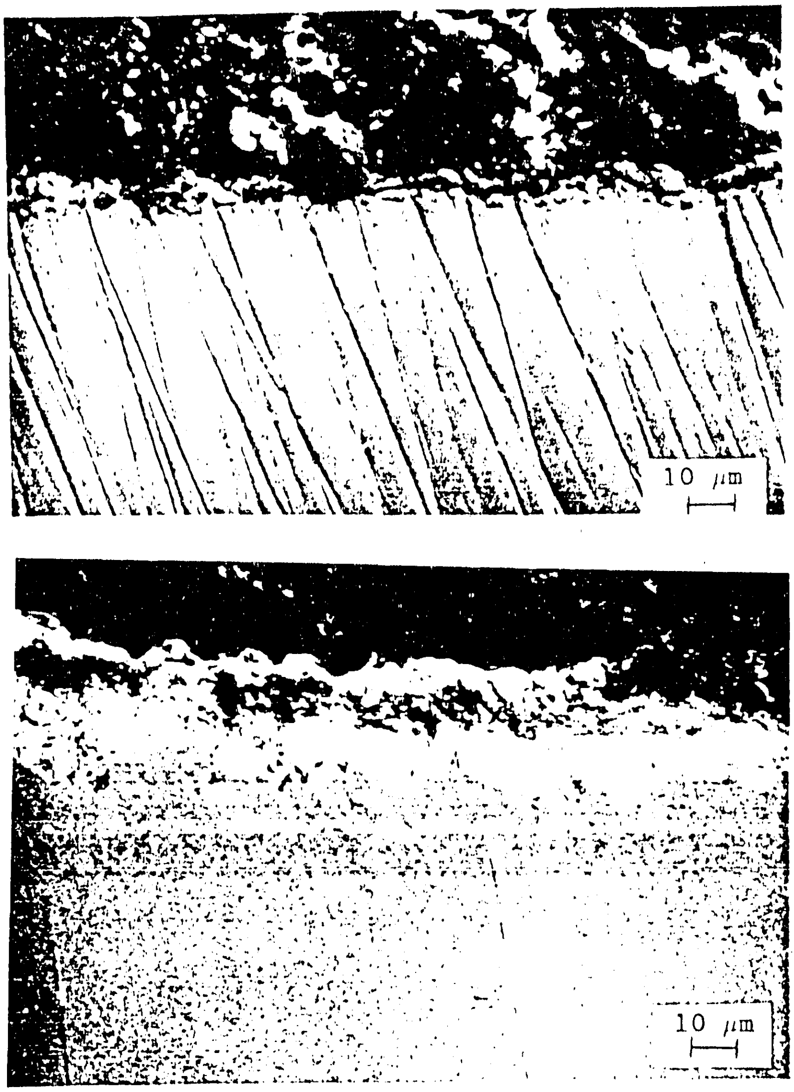

Figure 5 - Polished Cross Sections of Ni-Al Exposed for about 48 h to Static $NaNO_3$-KNO_3-Na_2O_2 at 650°C at APCI. (a) As-wrought. (b) Preoxidized.

Analyses of nickel aluminide exposed in the molten salt facility described above also revealed the presence of an aluminum-enriched surface layer.

Examination of polished cross sections of several Fe-(35-36 at. %) Al specimens by optical and scanning electron microscopy failed to reveal the presence of a contiguous corrosion product scale even when care was taken not to remove residual salt from a particular specimen and special polishing procedures were used. However, EDX showed aluminum enrichment along much of the surface. Isolated areas of aluminum-enriched material could be found in the salt layer. Aluminum enrichment was also detected by EDX when a cleaned Fe-35Al specimen surface was examined in normal view (rather than as a cross section). X-ray diffraction of several specimen surfaces after exposure and cleaning did not detect anything but the base material.

Salt Analysis

Table III shows the results of the chemical analyses of salt samples taken from crucibles containing iron aluminide specimens. Random samples of salt were taken after multiple exposures of specimens. One of these salts (3-2) was significantly more aggressive than the others and weight change results from exposures in this melt were not included in the above weight change results. Note that, for this atypical salt, the concentrations of Fe, Al, and Cr were all higher compared to the other salt samples and that it contained a relatively large amount of silicon. The reason for the unusual behavior of this salt is not known (possibly due to contamination from an O-ring) because it was prepared by the same methods as the other salt charges of similar starting composition. (It may have been related to contamination of the salt by an O-ring.)

Table III Analysis of Salt Samples from Crucibles (Atomic Absorption)

	Concentration (wt ppm)			
Element	2-2[a]	3-2[b]	3-3	4-2[c]
Al	<9.3	31	3.1	<10.0
Fe	3.8	170	<0.5	<2.1
Si	<37	130	13	54

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[a] First digit: crucible number; second: sequence number; Crucibles 2 and 3 contained Salts 1A and 1B.
[b] Atypical salt.
[c] Salts 2A and 2B.

Discussion

Earlier studies (17,18) have shown that weight change can differentiate the relative corrosion resistance of materials exposed to this aggressive nitrate salt where significant variances in susceptibilities exist. Such measurements as presented here clearly indicate that nickel and iron aluminides have better corrosion resistance in $NaNO_3(-KNO_3)-Na_2O_2$ salts than steels and nickel-based alloys (17,18). However, the crucible method employed in these studies does not directly lead to a mechanistic understanding of the corrosion process. Nevertheless, by combining the weight change data with thermodynamic information, salt analyses, and microstructural observations, the processes governing the relatively slow rate of corrosion in high-temperature $NaNO_3(-KNO_3)-Na_2O_2$ can be addressed.

As demonstrated previously (4-9), corrosion in molten nitrate salts can result both from solid-state oxidation of the base metal components and solubility-driven dissolution reactions. Therefore, weight change measurements must always be carefully analyzed. The measured weight change, w, can be expressed as

$$w = w_o - w_s - w_d - w_l \qquad (1)$$

where w_o is the weight gain due to the presence of oxygen in the specimen or its adhering scale, w_s is the absolute value of the weight loss due to dissolution of metal ions into the salt, and w_d and w_l are the weight changes caused by removal of any (or all) of the surface reaction product when rinsing the salt from the specimen after exposure (descaling, w_d) and/or by mechanical scale detachment at temperature or during cooling (spallation, w_l). Weight losses (negative w) indicate corrosive attack, but, by themselves, do not distinguish between that caused by dissolution (weight loss during exposure) or scaling (weight gain followed by loss due to descaling and/or spallation). Significant weight gains are indicative of corrosion associated with oxidation and scale formation. Relatively small weight changes do not necessarily mean a particular material is resistant to corrosion. If both dissolution and oxidation are occurring at rates such that oxygen uptake is approximately offset by metal ion dissolution, the net weight change would be small while the actual overall corrosion rate is substantial. However, in the present case of aluminides, there was no evidence of a residual corrosion product on, or salt-induced internal oxidation of, specimens exposed to the nitrates (see Figures 5 and 6). Therefore, w_o (the residual scale weight) must be small, so that, in many cases,

$$w \approx -(w_s + w_d + w_l) \qquad (2)$$

and small weight changes reflect relatively good corrosion resistance.

The absence of a residual scale does not mean that the aluminides were not oxidized. Indeed, since weight losses were normally higher when the salt was periodically refreshed with highly oxidizing Na_2O_2, it probably indicates that material was oxidized and dissolved into the salt (see below) and/or became detached during or after exposure. Thermodynamic calculations and microstructural analyses have shown that Fe_2O_3, $NaFeO_2$, and $NaAlO_2$ are the predominant reaction product species for iron- and aluminum-containing metals in these nitrate salt mixtures (6,10,11,16,18). In the absence of peroxide, exposure of iron to nitrate salt led to weight gains (11-14,18), thereby indicating formation of an insoluble corrosion product. [In contrast, a weight loss was measured upon exposure of iron to $NaNO_3$-Na_2O_2 (18).] Exposure of bulk alumina in Salts 1B and 2B produced small negative weight changes (see Table II) and suggests that $NaAlO_2$ forms but dissolves (albeit rather slowly) into the salt consistent with the presence of aluminum ions in the melt, as shown in Table III. [There is some indirect microstructural evidence for this product based on work with Fe-Ni-Cr-Al systems (18).]

When the aforementioned results for alumina are compared with relevant weight change data for the iron and nickel aluminides (Table II), it can be noted that the lowest weight losses of the alloys (that is, those near the minima of the respective scatterbands) are of the same order as those measured for alumina. This correlation, when considered with the other evidence discussed above, also seems to indicate that a slowly dissolving product layer involving aluminum forms on aluminides exposed to the aggressive nitrate salts and produces lower weight losses compared to many other alloys. The decreasing weight losses with increasing aluminum concentration of nickel and iron aluminides (Figure 2) indicate that the reaction products of iron and nickel are either more soluble or less mechanically compatible than $NaAlO_2$ over the basicity range of these experiments. This is consistent with the weight change findings regarding pure iron and Al_2O_3 exposures (discussed above) as well as with measurements for pure Ni (17,18), which showed significant weight losses. By being more corrosion resistant than the transition metal products, this slowly thickening (small w_o, w_d, w_l) and/or dissolving (small w_s) Al-containing layer thereby imparts a beneficial effect. The thin aluminum-enriched surface layers found on exposed nickel and iron aluminides could be evidence of a thin Al_2O_3 that should form under any $NaAlO_2$.

The salt analyses shown in Table III are also consistent with a model of a slowly dissolving $NaAlO_2$ layer that is controlling the overall corrosion process. Note that the concentration of aluminum ions was about the same for the three normal salt charges from which samples were taken, but for the atypical, more corrosive salt, iron was in much greater relative abundance. While the reason for the greater corrosivity of this salt is unknown, the end result was the inability of an aluminum-containing surface layer to hinder the movement of iron into the salt and correspondingly higher weight losses were measured. Assuming no change in corrosion mechanism between the typical and atypical salts, the correlation of increased concentrations of all the principal components of the exposed iron aluminides with weight loss indicates that solid material is lost into the salt principally by dissolution or in-salt spallation. In terms of Eq. (2), it is thus possible to conclude that $w_d \approx 0$ and that the principal contribution to w_l (if any) is from loss of scale into the salt.

The presence of aluminum in the salt and the increase in its concentration with increasing weight loss (Table III) suggest that it is not likely that the role of aluminum in the aluminides is to simply lower iron or nickel activity and diffusion rate in the alloys so that the corrosion process becomes selective removal of iron or nickel. However, the results of the salt analyses do not rule out a possible effect of aluminum as a solute in the salt that lowers iron and nickel solubility. In this case, the observed surface enrichment in aluminum would have to be due to selective removal of iron or nickel and the beneficial effect of increasing aluminum concentration would be due to a continuing decrease in the activity of iron or nickel in the alloy. Such a direct influence of iron/nickel activity on weight losses did not manifest itself in a dependence on the structure of the exposed aluminide: weight changes were insensitive to whether the aluminide was DO_3 or B_2. Furthermore, this solubility product model is inconsistent with the thermodynamic prediction of $NaAlO_2$ and the evidence for this product (18), as discussed above.

When Na_2O_2 was added to the salt at the beginning of an extended exposure period and not replenished, weight losses did not increase after about 24 h (Figure 4). Such observations illustrate the importance of the peroxide in reactions associated with the formation and loss of, presumably, $NaAlO_2$ and $NaFeO_2/Fe_2O_3$ (for iron aluminide). This is not unexpected; solubilities of oxides in the nitrate salt tend to be highly dependent on salt basicity (16,23), and it is reasonable that the addition of Na_2O_2 should significantly increase the solubility of these oxides in the basic dissolution regime (19). As noted above, in the presence of Na_2O_2, the weight change of pure iron switched from a gain to a loss. For basic dissolution of iron or aluminum (M) in the presence of Na_2O_2:

$$Na_2O_2 = 2Na^+ + O_2^{2-} \qquad (3)$$

$$K_3 = [a_{O_2^{2-}} \cdot (a_{Na^+})^2]/a_{Na_2O_2}$$

$$M_2O_3 + O_2^{2-} = 2MO_2^- + 1/2O_2 \qquad (4)$$

$$K_4 = [(a_{MO_2^-})^2 \cdot p_{O_2}^{1/2})]/(a_{M_2O_3} \cdot a_{O_2^{2-}})$$

where K_i and a_i represent equilibrium constants and chemical activities, respectively. Therefore, as Na_2O_2 is added to the melt, $a_{O_2^{2-}}$ increases [Eq. (3)] and, based on the dissolution reaction equilibrium represented by K_4, the concentration of MO_2^- in the salt (solubility) must increase. Alternatively, or additionally, the increased basicity due to the introduction of the peroxide can change the stable species (for example, Fe_2O_3 to $NaFeO_2$) and lead to increased dissolution and/or growth of a product that is less mechanically compatible with the base material (causing delamination). The observation that pure $NaNO_3$ is more corrosive than the mixed $(Na,K)NO_3$ salt (see Figure 3 and refs. 17 and 18) is consistent with a reaction process involving the formation of a sodium-containing product. The transitory effect of the peroxide additions (that is, the higher corrosion rate is only maintained if Na_2O_2 is refreshed) indicates that the peroxide is consumed and that it directly participates in, rather than simply accelerates, the corrosion process in agreement with the reactions described above.

At aluminum concentrations less than 28 at. %, nickel aluminide is slightly more resistant than iron aluminide (Figure 2), consistent with what is observed for nickel relative to iron in other nitrate salt systems (at lower temperature) (13,15) and with its generally lower rate constant in oxidizing gases (20). It is interesting to note, however, that this difference in corrosion resistance between the two aluminides is not found at higher aluminum concentrations when they are exposed to the present nitrate salts at 650°C (Figure 2). The iron and nickel aluminides show approximately equal corrosion susceptibilities despite differences in the oxidation kinetics of their respective transition metal components. This again indicates the important role of aluminum in controlling the corrosion process in the nitrate salt.

As described above, it is postulated that the $NaAlO_2$ layer inhibits the corrosion of the more susceptible products by preferentially forming on the surface and reducing the rate of iron or nickel transport into the salt to a level less than or equal to the (relatively low) rate at which aluminum is released. Thus, it is a competition between aluminum and the other principal alloy components that apparently determines the resistance of a particular aluminide composition to corrosion by $NaNO_3(-KNO_3)-Na_2O_2$. While the data of Figure 2 show that an aluminum concentration of at least 30 at. % appears necessary to afford improved corrosion resistance for iron aluminides, such a threshold for nickel aluminide cannot be ascertained from the present data for Ni-25Al and Ni-50Al. However, the similarities in average weight changes for NiAl and Fe-(>30 at. %) Al and the typical lower reactivity of nickel would seem to indicate a similar aluminum concentration for minimizing corrosion losses. The agreement between weight losses of nickel and iron aluminides at higher aluminum contents was further confirmed by results for a Fe-32Ni-32Al aluminide: the data fell in the same band as that shown in Figure 2 for Fe-30Al. On the other hand, TiAl is significantly more susceptible in the subject nitrate salt (see Figure 1) despite a high aluminum concentration. In this case, an even higher concentration of aluminum may be needed to lower corrosion rates to a level associated with control by surface $NaAlO_2$ because of the greater corrosivity of titanium in oxidizing environments (relative to iron and nickel). In view of such competition between the main components of the aluminides, increasing the aluminum concentration of iron and nickel aluminides to greater than 30 at. % certainly would not be deleterious to corrosion resistance and may actually be beneficial in case of any localized breakdown of the $NaAlO_2$.

Summary

The corrosion of aluminides by molten $NaNO_3(-KNO_3)-Na_2O_2$ was studied at 650°C. It was demonstrated that weight changes could be used to evaluate corrosion behavior of such materials in the subject nitrate salt environments and that weight losses were primarily caused by dissolution, and possibly spallation of any surface product, into the salt. These data were combined with salt analyses and the results from microstructural examinations to show that the corrosion of relatively resistant aluminides by these aggressive nitrate salts proceeded by oxidation and a slow release of ions from an aluminum-rich product layer into the salt at a rate lower than that associated with many types of metallic materials. The overall corrosion process and resulting rate were dependent on the particular aluminide being exposed. In order to minimize corrosion losses of nickel and iron aluminides, it was necessary to have aluminum concentrations in excess of 30 at. %. However, 50 at. % Al was not sufficient to improve the corrosion resistance of TiAl to even that of Ni_3Al and Fe_3Al. At higher aluminum concentrations, iron, nickel, and iron-nickel aluminides exhibited quite similar weight changes, indicative of the principal role of aluminum in controlling the corrosion process in $NaNO_3(-KNO_3)-Na_2O_2$ salts.

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